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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US94/09922 (22) International Filing Date: 29 August 1994 (29.08.94) (30) Priority Data: 145, 064 29 October 1993 (29.10.93) US (71) Applicant: UNION OIL COMPANY OF CALIFORNIA [US/US]; 1201 West Fifth Street, Los Angeles, CA 90017 (US). (72) Inventors: ALLEN, William, C.; 405 South San Marino Avenue, Pasadena, CA 91107 (US). STIKKERS, David, E.; 4650 Sierra Madre, Reno, NE 89502 (US). HOYER, Daniel, P.; 2197 Zinfindel, Santa Rosa, CA 95403 (US). (74) Agents: ABRAHAMMS, Colin, P. et al.; Ladas & Parry, Suite 2100, 5670 Wilshire Boulevard, Los Angeles, CA 90036 (US).	(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD). Published <i>With international search report.</i> 	
(54) Title: GLASS FIBER REINFORCED CEMENT LINERS FOR PIPELINES AND CASINGS		
(57) Abstract Cement liners for metal pipes include a fibrous material, such as glass fibers, to prevent cracking and/or inhibit crack propagation.		

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**GLASS FIBER REINFORCED CEMENT LINERS FOR PIPELINES AND
CASINGS**

BACKGROUND OF THE INVENTION

Field of the Invention

- 5 This invention relates to methods of lining pipes, and to pipes so lined, exposed to corrosive environments particularly to cement liners for metal pipe that carry corrosive fluids.

Background

- 10 Cement is used to line pipes that are conduits for corrosive or otherwise hard to handle compositions. One class of such corrosive compositions that must be transported through pipes is geothermal brines used to extract power from the earth. Although the cement used to line such pipes can be standard portland cement used without any special additives, many special cements are used for this purpose. For example, U. S. Patent 5,122,554, said patent incorporated by reference in full herein, describes enhanced
- 15 polymer concrete compositions. Polymer cements have the disadvantage of being more costly to produce than cements hydrated with water. However, water hydrated cements are subject to cracking caused by dry shrinkage during manufacture and storage, mechanical jarring during fabrication into pipelines, and corrosion and erosion during use as pipelines. The cracks propagate until they penetrate through the cement liner and
- 20 allow the corrosive contents of the pipe to contact the metal shell of the pipe, which, in turn, causes metal corrosion and the eventual failure of the pipe.

It would be advantageous to have a liner that was less costly to produce and did not crack or otherwise expose the supporting metal of the pipe to the corrosive contents of the pipeline.

SUMMARY OF THE INVENTION

According to one aspect of the invention, there is provided a lining for metal pipes comprising cement, between about 1 to 10 dry wt% glass fibers, and between 25 and 50 wt% silica flour added to the cement.

- with 2
- 5 According to another aspect of the invention, there is provided a method for making cement lined pipes comprising: hydrating a dry mixture comprising between 50 and 75 wt% cement and between 25 and 50 wt% silica flour enough to form a homogenous slurry; adding glass fibers; mixing the slurry until the glass fibers are evenly mixed throughout the slurry; and placing the cement slurry on the interior surface of metal
10 pipes.

According to a further aspect of the invention, there is provided a conduit for containing corrosive liquids comprising: an outer metal shell; and a cement lining attached to the interior surface of the shell, said lining including at least some fibers.

- A cement reinforced with micro fibers and/or macro fibers is preferably used to line
15 pipes. The pipes are typically lined with between about a 1/8 inch to 1/2 inch layer of the cement comprising between about 50 to 75 dry wt% cement, between about 1 to 10 dry wt% glass fibers, and 25 to 50 dry wt% silica flour. The pipes so lined are corrosion resistant, and, in particular, they are especially resistant to the corrosion caused by geothermal fluids.

- see 40
- 20 The corrosion resistant pipes may be made by adding enough water to a mixture of between 50 and 75 wt % cement, and between 25 and 50 wt% silica flour to form a homogenous slurry, adding glass fibers to the slurry and mixing the slurry with the added glass fibers until the glass fibers are evenly mixed throughout the slurry. The slurry may then be placed in a metal pipe and distributed on the interior surface of the
25 pipe. Preferably, if the pipe is cylindrical, it is rapidly rotated around its axis to evenly distribute the slurry on the inside surface of the pipe.

The pipes made by this invention preferably provide a conduit for containing corrosive liquids. The pipes may comprise a metal shell, and a cement lining usually between

about 1/8 inch and 1/2 inch thick in the interior of the metal shell. If the pipe is cylindrical and has been rotated, the glass fibers preferably form a stratum of high fiber concentration within the cement lining proximate the metal shell. Preferably, the metal shell is an elongate tube, and at least 30% of the glass fibers have their long dimension oriented within 30 degrees of the parallel to the plane of the local area.

DETAILED DESCRIPTION OF THE INVENTION

The cements useful in the present invention include portland type cements, particularly those identified by the American Petroleum Institute as G-type and K-type, two types of cement used primarily to finish oil wells. The ideal cement would have no change in dimension as it sets; however, real cements tend to expand (K-type) or shrink (G-type) during curing. The cement layer includes a fibrous material making the cement more resistant to crack propagation, and the pipes are lined with this material to better resist corrosion and failure. The added fibers stop the propagation of cracks within the cement. Other cements that can be used in this invention include the quick setting high alumina-content non-portland type cements.

Primarily because it expands as it cures, K-type cement is particularly preferred as the cement in this invention. Any cracks that might have been formed in the cement due to jarring or dry shrinkage, or other reasons, are squeezed out by the release of compressive strain resulting from the expansion of the cement upon cure. Although the added fibers tend to increase the tensile strength of K-type cement, they do not increase the tensile strength of G-type cement. However, G-type cement is useful in this invention because the fibers stop the propagation of cracks in the cement, rather than providing added tensile strength.

In addition to cement, fibers, and, of course, added water, the compositions of this invention also include a non-fibrous aggregate. The preferred non-fibrous aggregate used in the cement of the present invention is silica flour. The silica flour does not hydrate when the cement slurry is formed and comprises between about 85 wt% and 100 wt% silica particles (SiO_2) averaging from about 1 to 100 microns in size of particles of varying sizes. A typical mixture comprises 10% particles smaller than 3.2 microns, 50% smaller than 18.4 microns, and 90% smaller than 61.8 microns. The silica flour

provides added resistance to carbonation to the mixture. It is greatly preferred that the silica flour particles be as rough as possible, and silica flour made from smooth, round particles is preferably avoided. Between about one-half part and two parts, preferably between about three-quarters of a part and one and one quarter part, of silica flour is added to three parts of G-type cement, the parts measured as volume, and the two ingredients thoroughly mixed together as dry powders. Then, the mixture is hydrated with added water to make an aqueous slurry. Preferably, the fibers are then added to the aqueous slurry.

Preferred fibers can be either micro fibers or macro fibers. Micro fibers have a diameter between about $30\ \mu$ and $200\ \mu$ and an aspect ratio (the ratio of diameter to length) between about 20 and 500 to 1. Macro fibers have a diameter between about $50\ \mu$ and $500\ \mu$ and an aspect ratio between about 20 and 500 to 1. The ranges of dimensions for micro fibers and macro fibers as defined above overlap because any batch of fibrous material will contain a wide range of sizes of particles. However, micro fibers will have a median diameter of between about $100\ \mu$ and $125\ \mu$ and the macro fibers will have a median diameter between about $225\ \mu$ and $275\ \mu$. Preferred micro fibers include Wollastonite ($\text{CaO}\cdot\text{SiO}_2$) and preferred macro fibers include glass fibers. Although less preferred, other fibers of the same dimensions, for example, metal fibers, preferably metal fibers that resist corrosion such as titanium fibers, fibrous minerals, for example asbestos, and other fibers, such as graphite fibers, can also be used in the compositions of this invention. Preferred fibers will not hydrate in the slurry. The preferred macro fibers are fine glass fibers fused together into bundles of many parallel fibers. It is the bundles, not the individual component fibers, that have the preferred dimensions, including aspect ratios between 20 to 500 to 1, having diameters between about $30\ \mu$ and $200\ \mu$, and lengths between 3mm (approx. 1/8 in.) and 12 mm (approx. 1/2 in.). The preferred size is approximately 6mm having an aspect ratio between about 200:1 and 300:1. Sources of fibers meeting these specifications are, for the glass fibers, Chem-Fil Ltd.; Merseyside, England, U.K., and Thalco; City of Commerce, CA, U.S.A, and for the Wollastonite, Prescott & Co.; Mississauga, Ont., Canada. These fibers are added to the premixed slurry.

Although the fibers can be added at any time during the formulation of the cement, it is greatly preferred to add them to the cement slurry after the slurry has been premixed for between about 2 and 5 minutes. An amount between about 0.5 wt% and 10 wt%, the preferred amount being between about 1 wt% and 4 wt%, with about 1 wt% being the most preferred, of fibers are added to the cement, when the wt% is based on the weights of the dry materials. The preferred concentration of the preferred fibers is about 2 wt% of 6mm fibers. Higher concentrations of fibers, particularly higher concentrations of macro fibers, tend to result in the fibers clumping together in the slurry. This clumping creates a hard-to-handle slurry. Furthermore, the benefit of adding fibers seems to taper off for concentrations greater than 10 wt%. Therefore, it is preferred that the micro fibers be added to the slurry in the same concentrations as the macro fibers.

Although the invention is not bound by any particular theory of operation, it is now believed that, among other functions, the fibers help to distribute the stresses induced by the volume change of the cement as it cures. Shrinking occurs with non-expansive cements, typically occurring during the curing phase and varying with the cement used, the amount of water used in the cement slurry, and the extent of post cure drying. Shrinkage even occurs with expansive cements if the cement is allowed to completely dry in the post curing phase. Furthermore, cracks introduced from rough handling during storage and shipping are prevented from propagating by the addition of either the micro fibers or macro fibers.

Enough slurry is placed into the pipe to cover the interior surface of the pipe with between about 1/8 inch and 1/2 inch, preferably between 1/4 inch and 3/8 inch, cement slurry. If the pipe is cylindrical, it can be rapidly rotated around its longitudinal axis to distribute the slurry evenly throughout the interior of the pipe. In the case of the rotated pipe, the pipe is preferably rotated rapidly enough to generate a force of at least 1.5 G (where G is the force of gravity at the surface of the earth), and preferably greater than 2 G at the interior surface of the pipe. If the pipe is of some other configuration than cylindrical, the slurry can be spread by other conventional cement spreading means and left to cure.

The pipe joints and conduit made joining the pipe joints made by the method of this invention is characterized by an outer shell, preferably a metal shell, usually a steel pipe, with a cementitious layer lining the inside surface of the pipe. If the pipe is prepared by the rotating method outlined above the fibers added to the cement tend to form a stratum proximate the metal shell. The fibers of the spun pipes tend to lie parallel to a local plane defined by extending radii from the axis of the pipe to the liner, the angle between the radii not exceeding about 5 degrees. Although the local area is not planar, the fibers will be aligned to within about 30 degrees of the plane of the area. At least 30%, preferably 50%, and most preferably more than 60%, of the fibers in the stratum will be aligned to within about 30% of the local area.

The invention is further described by the following example, which is illustrative of various aspects of the invention and is not intended as limiting the scope of the invention as defined by the appended claims.

EXAMPLE

This example shows the use of the present invention to make several casing joints which were compared to joints made with conventional non-fibrous cements.

The cement was made by mixing 100 pounds of Type-G cement with about 40 pounds of silica flour and mixing batches using a paddle mixer. Fibers were added to the slurry in one pound, one and one half pound, and three pound amounts in both 6mm and 12 mm lengths after the slurry had been mixed for about two minutes. It was seen that the 3% fibers concentrations tended to form clumps and cause difficulties with the fabrication equipment. Enough of a batch of cement was placed into metal conduit to produce between a 1/4 inch and 5/8 inch lining. The resulting pipe section joints produced were stored for three to four weeks before installation. Then the joints were inspected by inserting a video camera down into the pipes. The video image showed significantly fewer cracks for the fibrous lined pipes than for similar pipes made with conventional, non-fibrous cement.

The joints were then placed into use at a geothermal brine production well and a geothermal brine injection well near the bottom of both well strings to test the most severe environment in both wells.

5 The preliminary analysis of the cement liners indicated that fiber concentrations greater than about 1 wt% seemed to interfere with the ability of the cement to bond with the metal liner. This is considered to be a rheology problem which allows the fibers to concentrate at or near the pipe/liner interface. The video inspection of the pipes indicated that fewer cracks had formed than would be expected for conventional pipes. Visual microscopic analysis of small sections of the liner indicated that the fibers in the
10 rotated liners are concentrated near the metal-to-liner junction, with a very high local loading of fibers, the local loading frequently being greater than 6%.

Although this invention has been primarily described in terms of a specific example and embodiments thereof, it is evident that the foregoing description will suggest many alternatives, modifications, and variations to those of ordinary skill in the art.
15 Accordingly, the appended claims are intended to embrace as being within the spirit and scope of invention all such alternatives, modifications, and variations.

CLAIMS

1. A lining for metal pipes comprising cement, between about 1 to 10 dry wt% glass fibers, and between 25 and 50 wt% silica flour added to the cement.
2. The lining of claim 1 wherein the cement comprises a G-type cement.
- 5 3. The lining of claim 1 wherein the cement comprises a K-type cement.
4. The lining of claim 1 wherein the fibers are macro fibers.
5. The lining of claim 4 wherein the macro fibers consist of bundles of fine glass fibers.
6. The lining of claim 1 wherein the fibers are micro fibers.
- 10 7. The lining of claim 6 wherein the micro fibers consist of Wollastonite.
8. The lining of claim 7 wherein the bundles of glass fibers are between 3 and 20 mm long.
9. The lining of claim 7 wherein the glass fibers are between 3 and 10 mm long.
- 15 10. The lining of claim 1 wherein the particles comprising the silica flour are between about 1 and 100 microns in diameter.
11. A method for making cement lined pipes comprising:
 - hydrating a dry mixture comprising between 50 and 75 wt% cement and between 25 and 50 wt% silica flour enough to form a homogenous slurry;
 - 20 adding glass fibers;
 - mixing the slurry until the glass fibers are evenly mixed throughout the slurry; and

placing the cement slurry on the interior surface of metal pipes.

12. The method of claim 11 wherein the pipes are cylindrical.

13. The method of claim 12 wherein the placing step comprises rotating the pipes rapidly enough to force the slurry onto the interior surface of the pipe.

5 14. The method of claim 12 further comprising the step of rotating the pipes rapidly enough to produce a force at least 1.5 G.

15. The method of claim 11 wherein the cement is G-type cement.

16. The method of claim 11 wherein the cement is K-type cement.

17. The method of claim 11 wherein the fibers are micro fibers.

10 18. The method of claim 17 wherein the micro fibers are Wollastonite fibers.

19. The method of claim 11 wherein the fibers are macro fibers.

20. The method of claim 19 wherein the macro fibers are bundles of fine glass fibers.

15 21. The method of claim 20 wherein the glass fibers are between 3 and 20 mm long.

22. The method of claim 21 wherein the glass fibers have an aspect ratio between about 200:1 and 300:1.

20 23. The method of claim 11 wherein the fibers are added after the slurry has been formed.

24. The method of claim 23 wherein the slurry is mixed for at least 2 minutes before adding the fibers.

25. The method of claim 11 wherein the slurry is mixed for at least five minutes before being placed on the interior surface of a pipe.

5 26. The method of claim 11 wherein enough cement lining material is placed in the pipe to result in a lining between about 1/8 inch and 1/2 inch thick.

27. A conduit for containing corrosive liquids comprising:
an outer metal shell; and
a cement lining attached to the interior surface of the shell, said lining
10 including at least some fibers.

28. The conduit of claim 27 wherein the outer metal shell is cylindrical.

29. The conduit of claim 26 wherein the conduit contains fibers forming a stratum within the cement lining proximate the metal shell, at least 30 % of the glass fibers having the long dimension oriented substantially parallel to the longitudinal axis
15 of the metal shell.

30. The conduit of claim 27 wherein the cement is cured G-type cement.

31. The conduit of claim 27 wherein the cement is cured K-type cement.

32. The conduit of claim 27 wherein the cement lining is between about 1/8 inch and 1/2 inch thick.

20 33. The conduit of claim 32 wherein the cement lining is between about 1/4 inch and 3/8 inch thick.

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 94/09922

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B28/04 F16L58/06 //(C04B28/04, 14:38, 14:42, 22:06),
C04B111:20, 111:56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,30 41 973 (MANNESMANN AG) 19 August 1982 see claims 1,2,10	1,10,27,28
A	---	11-13
X	GB,A,2 210 882 (BIO-KIL CHEMICALS LTD.) 21 June 1989 see page 1, line 1 - line 14 see page 6, line 19 - line 24 see page 7, line 1 - line 6 see page 7, line 27 - line 36 see page 9, line 27 - line 28	1,10
X	FR,A,2 351 346 (LECHLER CHEMIE GMBH) 9 December 1977 see claims 1,2	1,27,28,32

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 30 November 1994	Date of mailing of the international search report 15. 12. 94
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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